INTRODUCTION

Copper is one of the most abundant transition metals in atmospheric waters (Siefert et al., 1998). There are numerous measurements of total or dissolved copper in fog and rainwater; however, virtually nothing is known about the speciation of copper in atmospheric waters (Xue et al., 1991). Speciation is particularly important for copper because it exists in two oxidation states in natural waters, Cu(I) and Cu(II). Copper is involved in the redox chemistry of the atmosphere because of its reactivity with free radicals, such as $OH^{\cdot}$ and $HO_2\cdot$ (Xue et al., 1991). Copper is also involved in the redox chemistry of several trace metals including chromium and iron. A thorough understanding of redox conditions in atmospheric waters therefore must include a detailed understanding of copper speciation.

Siefert et al. (1998) found enrichment factors (using Al_{total} as the crustal tracer) for Cu_{total} that were greater than ten, indicating an anthropogenic source of copper to cloudwater. Furthermore, automobile traffic has been responsible for approximately 65% of the copper emissions in the United Kingdom (Sedlak, et al., 1997). Research in the last decade has demonstrated the importance of atmospheric deposition as an environmental pollutant transfer pathway (Scudlark et al., 1994). The ultimate environmental impact of this anthropogenic copper is unclear. One goal of this thesis is to determine if anthropogenic influences on the origin of an air mass impact the speciation of copper. This is essential to our understanding of the atmospheric reactivity and environmental fate of copper in the troposphere.

Copper is also an important component of estuarine systems, both naturally occurring and as a pollutant. Contamination by potentially toxic trace metals, such as

copper, contributes to the degradation of estuarine systems in North Carolina. Recent work demonstrates that speciation (the distribution of a metal among its various chemical forms) is an important control on the geochemical fate and cycling of copper in the Cape Fear estuary (Shank, 2003).

EXPERIMENTAL

Sample Collection

Rainwater

Rainwater samples were collected on an event basis at the University of North Carolina at Wilmington campus rainwater collection site from August 25, 2000 to September 24, 2002. The UNCW rainwater collection site is a large open area, approximately one-hectare, within a turkey oak, long leaf pine, and wire grass community, typical of inland coastal areas in southeastern North Carolina. This rainwater site (34^{o}13.9'N, 77^{o}52.7'W) is approximately 8.5 km from the Atlantic Ocean. There are over 15 years of rainwater composition data for this site, which was useful in interpretation of the data generated and also allowed comparison with other locations. Due to the close proximity of the collection site to the laboratory, Cu(I) analyses could be initiated within minutes of collection, which reduced the possibility of compositional changes between the time of collection and analysis.

Event rain samples were collected using four Aerochem-Metrics (ACM) Model 301 Automatic Sensing Wet/Dry Precipitation Collectors (Figure 1). One of the collectors contained a 2 L muffled Pyrex glass beaker from which samples for dissolved organic carbon (DOC), hydrogen peroxide, pH, and inorganic ions were collected. The trace metal sample collectors consist of a Teflon funnel connected by Tygon tubing to a 2 L

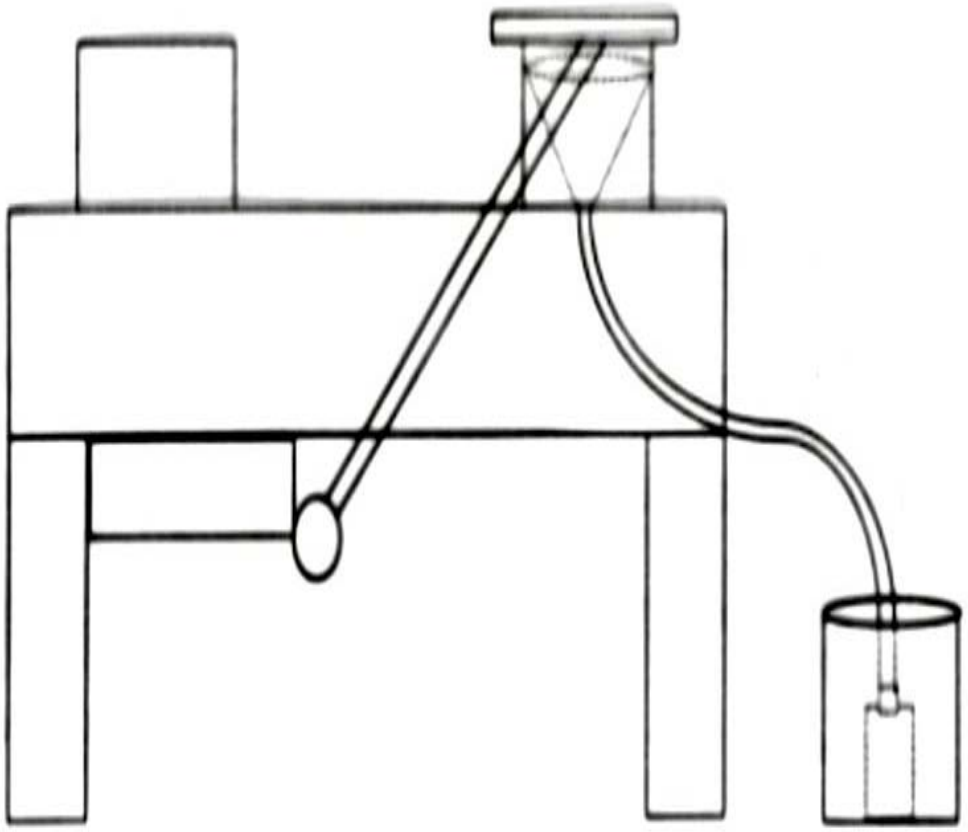


Figure 1. Aerochem Metrics Model 301 Automatic Sensing Wet/Dry Precipitation Collector

Teflon bottle extensively cleaned using trace metal clean procedures and protocols (Bruland et al., 1979; Bruland, 1980; Tramontano et al., 1987; Williams et al., 1998). Rainwater that was analyzed for Cu, Cr, and Fe was taken from these trace metal collectors. Meteorological data including rain amounts, rain duration, time of day, surface temperature, wind speed, wind direction and storm origin were also recorded. Real time precipitation maps were used to define the end of specific rain events, which initiated the sampling process.

Estuarine Water

Estuarine water samples were collected during April, July, and November of 2001 and March 2002. These dates were chosen to determine if seasonality affects copper speciation. Sediment and water sampling was conducted at two sites along the Cape Fear River, which drains the largest river basin in the state of North Carolina. Each is located in different salinity and water chemistry regimes (low salinity waters with a significant blackwater component *vs.* high salinity waters with a significant seawater component). The lower estuary site is located adjacent to the Southport ferry terminal. The upper estuary site is located adjacent to the Port of Wilmington (POW), one of two major commercial shipping terminals in the state. Both study sites showed preliminary evidence of contamination with metals, based on previous studies (Röhl, 1980; Mallin et al., 2001).

Copper(I) fluxes were measured using a core incubation technique described by Burdige and Homstead (1994), modified for trace metals as described in Skrabal et al. (1997). In this approach, a box corer deployed off UNCW's 19 m research vessel, the R/V Cape Fear, collected undisturbed bottom sediments in the estuary. The box cores were carefully subcored using acrylic core tubes (~14 cm diameter, ~60 cm long), sealed

at the bottom with plastic core caps, and covered with acrylic cover plates fitted with sealable sampling ports. Three to six cores were taken at each site. The cores were transported carefully back to the laboratory in an insulated box, where they were incubated at *in situ* temperature and in the dark.

Before beginning a flux experiment (typically within 24 h of return to the laboratory), the water overlying the cores was flushed using a peristaltic pump with ~3 volumes of ambient (recharge) water which was collected at the same time as the cores and stored in a polyethylene carboy under the same light and temperature conditions as the cores. The water level in the cores was adjusted to 8-13 cm above the sediment surface, with a slight space left between the overlying water level and the core top. The volume of water overlying the core was then approximately 1.2 to 1.9 L. Filtered air was gently bubbled into the water overlying the core using small diameter Teflon tubing inserted through the cover plate. The air gently mixed the water and maintained its O_2 concentration at near-ambient levels, with negligible loss of CO_2 (Burdige and Homstead, 1994).

Samples of water (500 mL) overlying the core were removed initially and after 48 hours using a syringe and Teflon tubing inserted into the sampling pore on the cover plate. Withdrawn volumes were replaced by equal volumes of ambient water. Samples for Cu(I) were also taken from the recharge water to account for any possible changes occurring during storage. Samples were immediately filtered through Missner 0.2 μm polyethersulfone membrane filters.

Analytical

The Cu(I) extraction (Moffett and Zika, 1988) was done the same way for both rainwater and estuarine water samples, with the only difference being the preconcentration was larger with the estuarine water.

Rainwater

Copper redox speciation was determined by quantifying Cu(I) concentrations in a freshly collected rainwater sample using a solvent extraction method. This method was chosen because the Cu(I)-specific chelator 2,9-dimethyl-1,10-phenanthroline (dmp) and Cu(I) complex are water soluble yet readily extracted into certain solvents. Methylene chloride was chosen as the solvent because the Cu(I)-dmp complex is readily extractable into it and because naturally occurring Cu(II) organic complexes, which would interfere with the Cu(I) determination, were not extracted. Ethylenediamine (en) was added to complex Cu(II) and prevent its reduction. The method has a detection limit of 0.015 nM (Moffett and Zika, 1988). The relative standard deviation for the rain and estuary water replicates was approximately 7% and 14%, respectively.

The sampling efficiency, on an event basis, was approximately 39% for all copper forms (Cu(I), total Cu, dissolved Cu). Not all rain events were sampled because some lacked sufficient volume and/or too much time expired between collection and analysis.

Due to the rapid oxidation of Cu(I), samples must be collected and analyzed within four hours after the rain event stops. One sample analyzed twelve times in four hours after sampling showed no change (ANOVA, $P = 0.303$), however, two samples analyzed immediately and after twenty-four hours both decreased in Cu(I) concentration by more than 50%. Another did not change after twenty-four hours. Copper(I) recovery

experiments were performed with fresh, authentic rain samples. Both recovery experiments showed a 48% recovery of Cu(I) (Table 1). All rainwater Cu(I) values are corrected for this recovery. For recovery experiments a fresh, nitrogen purged Cu(I) solution was made by dissolving cuprous bromide in a 1 M NaCl/0.005 M HCl solution. The solution was placed in a 50^{o}C water bath for 30 minutes to enhance dissolution (Moffett and Zika, 1983). Three fresh rain samples were spiked and three were left unspiked. The spiked samples were spiked with approximately 10 nM Cu(I). Both sets of extractions were done in triplicate and with the same experimental technique. Therefore, the values in Table 1 represent an average concentration. Values of pH, H_2O_2, DOC and Cl^- are shown in Table 1 to indicate the difference between these two rain events.

In another analytical test, an inorganic Cu(II) concentration of 1 nM was spiked into synthetic rainwater (pH 4.5 MilliQ, prepared by diluting 4 mL of 5 mM H_2SO_4 to 1 L with MQ water) which was extracted for Cu(I). No inorganic Cu(II) was extracted, again confirming the selectivity of the extraction.

Three sample aliquots of 250 mL were filtered within 10 minutes of collection through an acid cleaned 0.2 μm Millipore Isopore membrane filter and placed into fluorinated polyethylene bottles, which were cleaned extensively using trace metal clean techniques (Bruland et al., 1979; Bruland, 1980; Tramontano et al., 1987; Williams et al., 1998). All samples were filtered in a class 100 laminar flow clean bench to minimize sample contamination. The three 250 mL aliquots were then transferred to separate 250 mL separatory funnels. A volume of 0.5 mL of a stock solution, consisting of 2.5 mM dmp and 12 mM en adjusted to pH 8, was added to each separatory funnel. After 10

Table 1. Cu(I) recovery experiments with filtered offshore water and fresh rain. Concentration of unspiked samples are corrected using % recovery of Cu(I).

Date of rain/offshore water	unspiked sample(nM)	spiked sample(nM)	spike(nM)	% recovery	pH	DOC (uM)	H_2O_2 (uM)	Cl (uM)
3/13/2002 Rain	0.54	5.06	10	48	5.98	16	18	15
6/18/2002 Rain	1.7	5.58	9.9	48	4.51	135	3	36
2/1/2002 Offshore	0.12	4.5	10	44	N/A	N/A	N/A	N/A

seconds of mixing, 20 mL of HPLC grade methylene chloride was added to each funnel. This was shaken for 30 seconds and the phases allowed to separate (about 1 minute). The solvent, which contains the Cu(I)-dmp complexes, was transferred to three different 125 mL separatory funnels and 2 mL of 5% nitric acid added. Each 125 mL funnel was shaken vigorously for 30 seconds and allowed to separate (about 10 minutes). The 2 mL nitric acid layer was drained into a small vial and capped. This procedure effectively preconcentrated the copper 125-fold for rainwater and 250 fold for estuary water. The copper concentration in the extracted samples was analyzed by graphite furnace atomic absorption spectroscopy (GFAAS), using a Perkin Elmer 5100 PC Atomic Absorption Spectrometer equipped with a 5100 ZL Zeeman Furnace Module and AS 70 autosampler. Table 2 shows the temperature program used with the 5100 PC Atomic Absorption Spectrometer.

Total and dissolved copper concentrations were measured using standard additions combined with GFAAS multiple injections and non-boiling evaporation preconcentration (Görlach and Boutron, 1990). Two 30 mL samples were taken from each rain event. One sample was filtered for determination of total dissolved copper, and the other was left unfiltered for determination of total copper. A volume of 100 μL of Optima HCL (Fisher) was added, after filtration, to each sample and samples were refrigerated until analysis. Particulate copper was determined by the difference between filtered and unfiltered samples. The non-boiling evaporation preconcentration technique evaporated a 15-20 mL rain sample down to 50-100 μL. One milliliter of 5% HNO_3 was then added and allowed to sit in the 30 mL Teflon vial for a minimum of 10 minutes.

Table 2. Graphite Furnace temperature program for the analysis of copper.

Step	Temperature(^{o}C)	Ramp(sec)	Hold(sec)
1	110	1	30
2	130	15	30
3	1200	10	20
4	2000 (stop flow)	0	5 (read)
5	2400	1	2

The sample was then drained into a trace metal clean vial and analyzed by GFAAS within 24 hours.

To confirm the accuracy of the non-boiling evaporation preconcentration technique blanks and a standard reference material were analyzed (Table 3). With each group of samples a synthetic rainwater blank was evaporated in the same manner as the authentic rainwater samples. The average measured concentration of these synthetic rainwater blanks was 0.3 $\pm$ 0.2 nM. Four replicates of a riverine standard reference material (National Research Council of Canada, SLRS-4) with a certified concentration of 28.48 $\pm$ 1.26 nM were evaporated and analyzed. The average measured concentration of these replicates was 25.2 $\pm$ 1.8 nM.

Estuarine Water

Copper(I) recovery experiments were performed with filtered offshore water (Salinity = 36) that was collected in February of 2002. The primary Cu(I) stock used was prepared like the primary Cu(I) stock used for the recovery experiment in rain (described above). However, dmp and hydroxylamine hydrochloride were added to the secondary Cu(I) stock when spiking the offshore water. These reagents kept the copper stable and in its reduced form. Two samples were spiked and two were unspiked. The spiked samples were spiked with approximately 10 nM Cu(I). Both sets of extractions were done in the same way. The experiments showed a 44% recovery of Cu(I) (Table 1). All estuarine Cu(I) values are corrected for this recovery. Moffett and Zika (1988) found a Cu(I) yield of 80 $\pm$ 5% when spiking Biscayne Bay water. The reasons for the lower recovery in the present work are not known. However, the Cu(I) recovery found for the offshore water (44%) is consistent with the recovery found for rainwater (48%).

Table 3. Recovery experiment with the non-boiling evaporation preconcentration technique. The concentration of the riverine standard reference material (SLRS-4) is 28.48 $\pm$ 1.26 nM. Synthetic rain is pH 4.5 MilliQ water made by diluting 4 mL of 5 mM H_2SO_4 to 1 L with MilliQ water.

	Measured Concentration(nM)
Synthetic Rain Blanks	0.3 $\pm$ 0.2
Riverine Standard Reference Material	25.2 $\pm$ 1.8

Supporting Data

Rain samples were analyzed for Cl^-, NO_3^-, SO_4^{2-}, and PO_4^{3-} using ion suppressed chromatography (EPA, 1981; Fitchett, 1983). Analysis of pH was conducted using a Ross electrode with low ionic strength buffers (McQuaker et al., 1983; Boyle, 1986). Hydrogen peroxide was measured by fluorescence decay (Kieber and Helz, 1986). All statistical analysis was done with the software SigmaStat (SigmaStat, 1997). C. Shank provided the estuarine water total copper concentrations (unpublished data).

RESULTS AND DISCUSSION

Rainwater was collected in Wilmington, North Carolina from 68 storms between August 25, 2000 and September 24, 2002. Volume weighted averages for Cu_{total} (dissolved plus particulate), Cu(I), and Cu(II) were 5.3 $\pm$ 0.9 nM, 1.4 $\pm$ 0.2 nM, and 3.2 $\pm$ 0.9 nM, respectively (Table 4). This is the most comprehensive set of speciation data for copper in rainwater.

The volume weighted average concentration of Cu_{total} in Wilmington rainwater was approximately 5 nM, which is similar to the copper concentrations determined by Scudlark et al. (1994) in rain from the Maryland shore of the Chesapeake Bay (4 nM) and the same as the total copper concentration, 5.0 nM, determined by Church et al. (1984) in Bermuda rainwater. Campos et al. (2001) determined a total dissolved copper concentration of 6.4 nM for rainwater at an urban site in Brazil (Table 5). Hofmann et al. (1991) found relatively high concentrations of copper at an urban (29.4 nM) and rural (28.2 nM) site in Germany. It is difficult to compare the values determined by Hofmann et al. (1991) because of the small number of samples (one at each site). More recently, Halstead et al. (2000) determined a total copper concentration of 0.2 nM in Fiordland,

New Zealand. The smaller volume weighted total copper concentration determined in New Zealand may be due to less landmass around this remote sampling site. Total copper concentrations in cloud and fog water are higher than rainwater (Table 5). Cloud and fog waters are more concentrated systems, with smaller volumes and lower pH values.

The majority of copper in Wilmington rain was dissolved (Table 6). Chester et al. (1997) found copper to be 76% dissolved, more than any other rainwater metal they studied. This is similar to the 65% dissolved copper that was found in cloudwater in Great Dun Fell, U.K. (Sedlak et al., 1997). Twenty-six percent of the total copper in Wilmington rain was Cu(I). This matches closely with the percentages of Cr(III) and Fe(II) determined in Wilmington rain (Table 6). Twenty-four percent of the total chromium was Cr(III) (Kieber et al., 2002) and 16% of the total iron was Fe(II) (Kieber et al., 2001) in Wilmington rainwater. Although no copper speciation studies were done in rainwater, Xue et al. (1991) determined that Cu(I) represented between 4 and >90% of the total copper found in fogwater in Dubendorf, Switzerland, a suburb of Zurich.

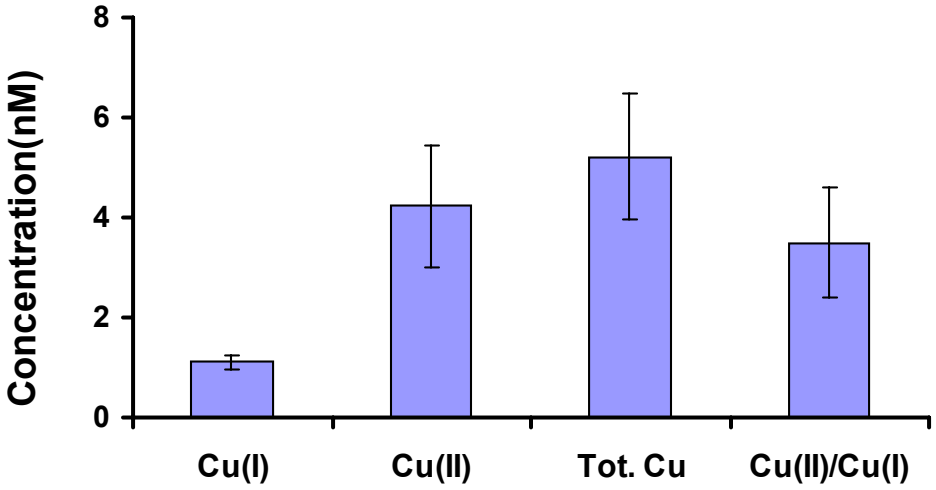
Seasonality

All rain events were separated into winter and summer seasons. The winter season was defined as December 1 – February 28, whereas the summer season was defined as June 1 – September 30. Copper(II) concentrations were significantly higher ($p = 0.003$) in summer months relative to Cu(I) with a Cu(II)/Cu(I) ratio of 3.5 (Figure 2a). In contrast to summer, Cu(I) concentrations were significantly higher ($p = <0.001$) than Cu(II) concentrations in the winter with a Cu(II)/Cu(I) ratio of 0.2 (Figure 2b). There was a statistically significant difference between the Cu(I) summer and winter values ($p =$

Table 6. Percentages of Cu(I), Cr(III), and Fe(II) relative to total Cu, Cr, and Fe in Wilmington, NC rain. Percentages of dissolved Cu, Cr, and Fe. The oxidized:reduced ratio for dissolved Cu, Cr, and Fe. Chromium data obtained from Kieber et al. (2002). Iron data from Kieber et al. (2001).

	% Reduced Form of Total	% Dissolved of Total	Oxidized:Reduced Ratio
Cu	26	96	2.3
Cr	24	52	1.2
Fe	16	26	0.7

a. Summer rainwater from 2000 – 2002



b. Winter rainwater from 2001 - 2002

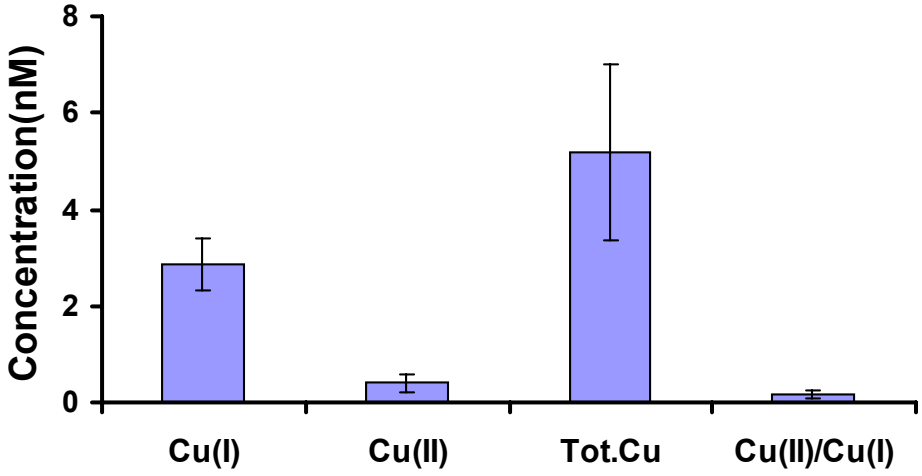


Figure 2. Volume weighted averages and standard deviations for Cu(I)(aq), Cu(II)(aq), Cu total and Cu(II)/Cu(I) ratio.

<0.001); however, both these seasons had a large range of data for Cu(II) and were not statistically different ($p = 0.097$). Total copper concentrations remained unchanged between the seasons. This suggests that the increase of Cu(II) seen in the summer occurs at the expense of oxidation of Cu(I), whereas in the winter Cu(I) is found as a result of Cu(II) reduction.

Rainwater contains both oxidants (H_2O_2, dissolved O_2, free radicals) and reductants (Cr(III), Fe(II), H_2O_2, NH_4^+). The increase of Cu(II) in the summer indicates the predominance of Cu(I) oxidation processes whereas the increase of Cu(I) in the winter suggests rainwater is a more reducing environment for copper during this time. The higher concentrations of Cu(II) in the summer and Cu(I) in the winter agree with results found for Cr(III) and Cr(VI) in our laboratory (Kieber et al., 2002). Chromium(VI) concentrations (1.4 ± 0.5 nM) were significantly higher ($p<0.03$) in the summer months relative to Cr(III) concentrations (0.7 ± 0.2 nM). Cr(III) concentrations (1.3 ± 0.3 nM) were significantly higher (t-test, $p<0.001$) than Cr(VI) concentrations (0.6 ± 0.2 nM) in the winter. Like total copper concentrations, total chromium concentrations remained unchanged between the seasons. Iron seasonality was also studied in our laboratory. The rainwater concentrations of Fe(III) were higher in the spring and summer relative to the autumn and winter ($p < 0.05$ for both ANOVA and t-testing) (Willey et al., 2000). Therefore, Cu(II), Cr(VI), and Fe(III) all showed increased concentrations during the summer in Wilmington rainwater. This indicates a more oxidizing environment may be present in the atmosphere during the summer. Fe(II) did not vary significantly between summer and winter (ANOVA, $p = 0.43$) and Fe_{total} was higher in the spring and summer relative to the autumn and winter ($p < 0.001$) (Willey et al., 2000).

Impact of Storm Origin

Rain events were subdivided based on storm origin as either coastal, continental, or other. All volume weighted copper concentrations (Cu(I), Cu(II), Cu_{total}, $Cu_{particulate}$) were higher for storms of continental origin versus storms of coastal origin (Table 4). The Cu(I) concentration for continental storms, which included cold fronts and continental lows, was 2.2 $\pm$ 0.3 nM. Copper(I) concentrations for coastal storms, which included coastal lows, winter warm fronts, hurricanes and tropical storms, was 0.9 $\pm$ 0.2 nM. The other storm origins category included mixed stationary fronts and local thunderstorms. Copper(II) concentrations for continental and coastal storms were 7.7 $\pm$ 2.1 nM and 1.9 $\pm$ 1.2 nM respectively. Concentrations of Cu_{total} for continental and coastal storms were 10.2 $\pm$ 2.0 nM and 3.4 $\pm$ 1.5 nM respectively (Table 4). Copper levels in continental rainwater may be higher because storms accumulate additional copper as they pass over large landmasses. This total copper increase may explain the increase in Cu(I) and Cu(II) for storms of continental origin.

Correlation Analysis

Correlation analysis was performed between copper concentrations and other rainwater analytes in order to evaluate patterns of variation. Copper(I) correlated significantly with $Cu_{particulate}$ and Cu_{total}, but not with Cu(II). Copper(II) did not correlate with any rainwater analytes, except Cu_{total} ($r = 0.676$). Significant positive correlations were found between Cu(I) and DOC, NO_3^-, SO_4^{2-}, Fe_{total}, and $Fe_{particulate}$ (Table 7). Concentrations of nitrate and sulfate were intercorrelated in the current study and in previous studies at this location (Willey and Kiefer, 1993; Willey et al., 1996) as well as in other locations in the eastern United States (Gorham et al., 1984; Hooper and Peters,

Table 7. Correlation values (r values) for rainwater analytes that showed significant positive correlations. n is greater or equal to 50 for all correlations, except for Fe_{total} (n = 22) and $Fe_{particulate}$ (n = 21). p is less than 0.005 for all correlations, except for $Fe_{particulate}$ (p = 0.015). Asterisks indicate no significant positive correlation.

	Cu(I)	$Cu_{particulate}$	H^+	NO_3^-	SO_4^{2-}	DOC	Fe_{total}	$Fe_{particulate}$
Cu(I)		0.390	*	0.591	0.596	0.374	0.593	0.525
Cu_{total}	0.487	0.730	0.366	0.577	0.598	0.356	*	*

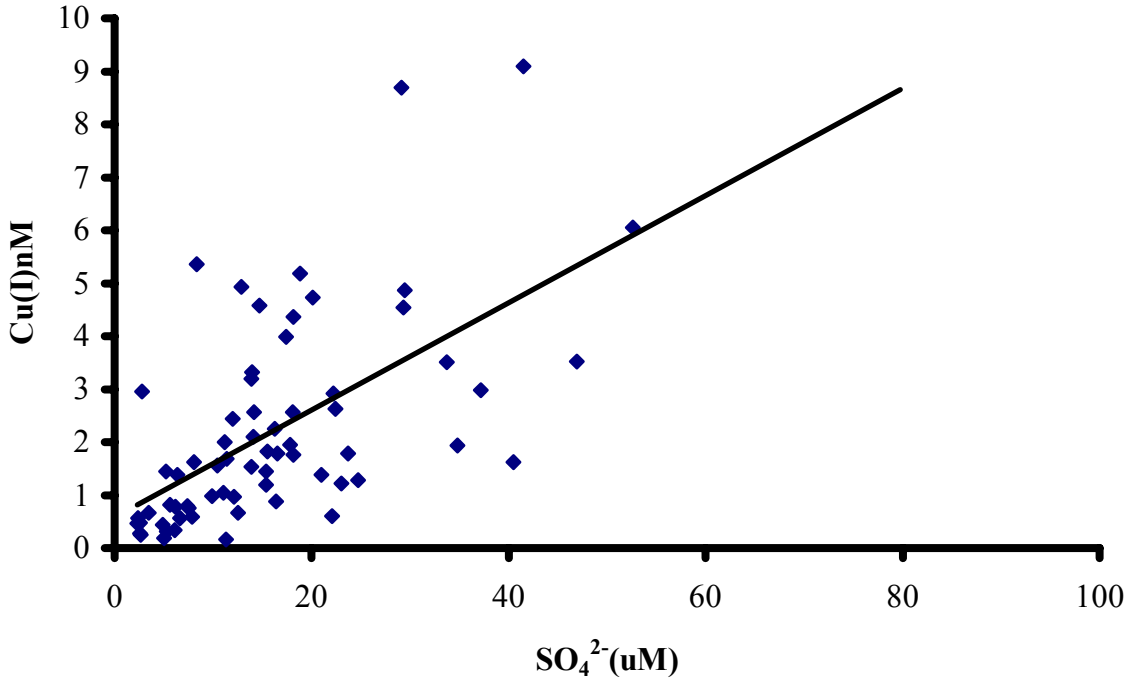
1989). The correlation between NO_3^- and SO_4^{2-} has been interpreted as reflecting their common anthropogenic sources, and hence they are often used as pollution indicators in rain. Copper(I) was highly correlated with NO_3^- ($r = 0.591$, $n = 67$) and SO_4^{2-} ($r = 0.596$, $n = 67$) in this study. Figures 3a and 3b show scatter plots of Cu(I) versus SO_4^{2-} and Cu(I) versus NO_3^-, respectively. The intercorrelation of Cu(I) with pollutant components suggest a possible anthropogenic input of Cu(I). Automobile traffic has been responsible for approximately 65% of the copper emissions in the United Kingdom (Sedlak et al., 1997). Using NO_x, a precursor to NO_3^-, as a tracer for road traffic emissions, Harrison et al. (2003) found a significant correlation between copper and road traffic emissions. Therefore, a possible pollutant source of Cu(I) is motor vehicle traffic.

Total copper and rain amount showed an inverse correlation. This indicates simple washout and dilution of copper as the volume of rain increases (Figure 4). Helmers and Schrems (1995) observed washout for rainwater copper that fell over the equatorial Atlantic Ocean and South Atlantic Ocean. Copper(I), Cu(II), and $Cu_{particulate}$ showed an inverse correlation with rain amount similar to total copper. H_2O_2, Cl^-, Cr_{total}, $Cr_{particulate}$, Cr(III), Cr(VI), Fe(II), and Fe(III) did not show a significant correlation with any copper species.

Year 1 and Year 2

All rain events were separated into year 1 (August 25, 2000 – September 23, 2001) and year 2 (September 24, 2001 – September 24, 2002) for purposes of comparison (Table 4). The number of samples (n) analyzed for each copper species for year 1 versus year 2 is approximately the same, Cu(I) being the exception. The most obvious difference between year 1 and 2 is the Cu(II) and Cu_{total} concentrations. Cu(II) is 60

a. Cu(I) (nM) versus SO_4^{2-} (μM)



b. Cu(I) (nM) versus NO_3^- (μM)

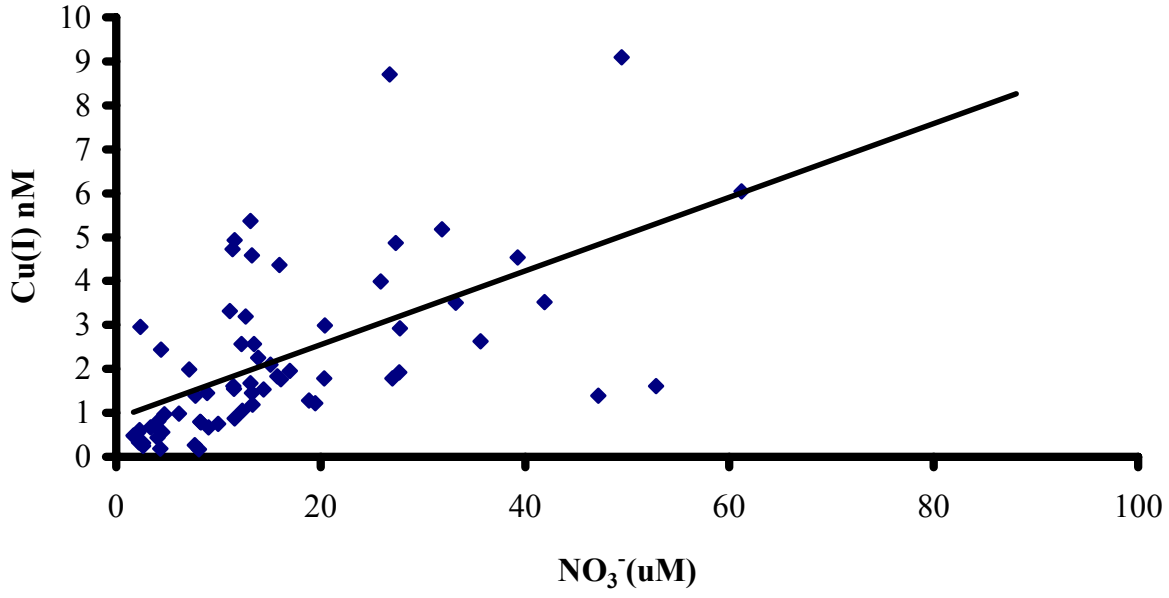


Figure 3. Cu(I) (nM) versus SO_4^{2-} (μM) and NO_3^-(μM) in Wilmington, NC rain.

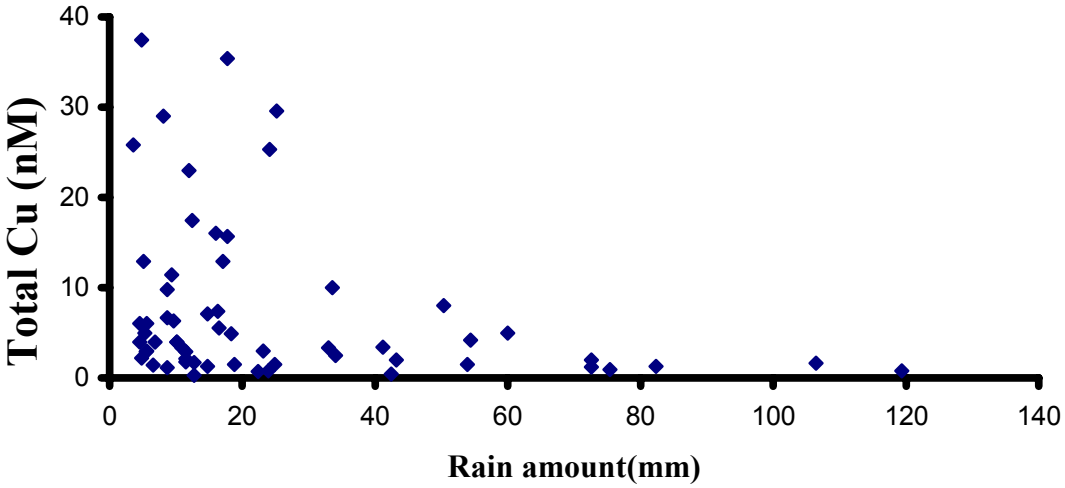


Figure 4. Total Cu (nM) versus rain amount (mm) for Wilmington, NC rainwater.

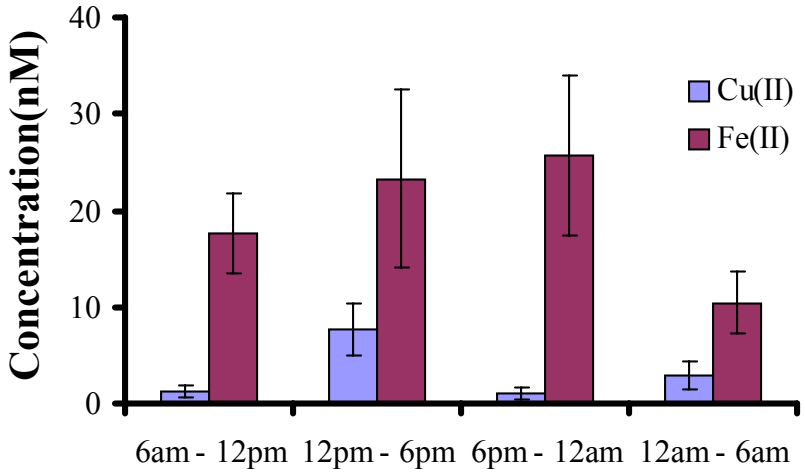
times higher in year 1 than 2 and is the major influence on Cu_{total} year 1 values being higher than year 2. For Cu(II) year 1, 45% of the storms were of continental origin, however, only 15% were of continental origin for Cu(II) year 2. Rainwater that has a continental origin usually contains higher copper concentrations, therefore, this may explain the higher Cu(II) and Cu_{total} values for year 1. Copper(I) and $Cu_{particulate}$ were higher in year 1 than 2, but the difference was not as pronounced as Cu(II) and Cu_{total}. Copper(II) makes up 83% of the Cu_{total} for year 1, therefore, the smaller difference between Cu(I) and $Cu_{particulate}$ for year 1 versus 2 is logical because Cu(II) dominates the copper concentrations.

Diurnal Variations

All rain events were subdivided based on time of day during which the rain event occurred. Days were divided into four time periods from 6 am-12 pm, 12 pm-6 pm, 6 pm-12 am, and 12 am-6 am local time. There are diurnal oscillations in Cu(II), Fe(II), and Fe(III) when these analytes are plotted versus time of day (Figure 5a and 5b). For the time periods 6 am – 12 pm to 12 pm – 6 pm there are increases in Cu(II) and Fe(II), with a simultaneous decrease in Fe(III). In contrast, from 12 pm – 6 pm to 6 pm – 12 am there is a decrease in Cu(II) with a simultaneous increase in Fe(III). It is possible that iron oxyhydroxides with adsorbed Cu(II) undergo reduction that releases Cu(II) in the presence of sunlight (Behra and Sigg, 1990; Faust, 1994). Iron oxyhydroxides can be reduced to the more soluble Fe(II) form with the sequential release of Cu(II).

$$FeOOH(s)/Cu(II) + h\nu + DOC \rightarrow Fe(II)(aq) + Cu(II)(aq)$$

a. Cu(II) and Fe(II)



b. Cu(II) and Fe(III)

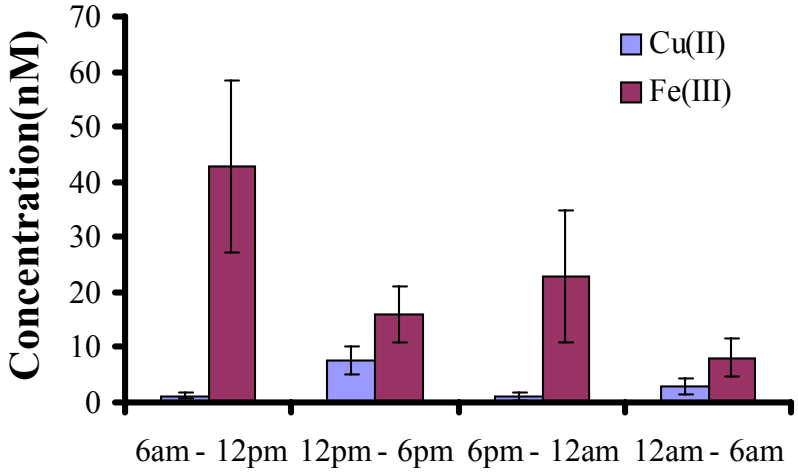


Figure 5. Volume weighted averages and standard deviations for Cu(II), Fe(II), and Fe(III) versus time of day.

Copper(I) concentrations were relatively constant over a 24 hour period (Figure 6), in contrast to the fog and stratus cloud chemical kinetic model of Siefert et al. (1998) that predicted Cu(I) should increase during daylight conditions.

pH dependence

All rain events were separated based on pH categories. Values of pH were divided into three categories: $pH \geq 4.95$, $4.55 \leq pH \leq 4.94$, and $pH \leq 4.54$ (Table 8). All copper concentrations (Cu(I), Cu(II), Cu_{total}, $Cu_{particulate}$) increased with decreasing pH (Figure 7). Chester et al. (1997) determined Cu_{total} becomes more soluble at lower pH values when analyzing rain from the Western Mediterranean coast. For Wilmington, NC rainwater these results may reflect difference in storm origin because continental storms, which contained relatively high concentrations of copper compared to coastal storms, usually had lower pH values.

Copper Stability in Rainwater

Synthetic rainwater was spiked with 4.8 nM Cu(I) and duplicate extractions were done within minutes (Figure 8). The Cu(I) oxidized quickly and only 0.1 nM was recovered. Authentic rain samples were extracted for Cu(I) within minutes, after 4 hours, and after 24 hours after collection. Rain samples were 0.2 μm filtered into trace metal clean bottles. The t(4) samples were placed in a dark cabinet at room temperature and the t(24) samples were placed in the refrigerator. Triplicate analyses were done for all three time points and concentrations were averaged. Over a 24 hour period, the Cu(I) concentration in authentic rain decreased by only 19%. These two studies indicate the presence of some stabilizing constituent. Similar stability was observed for Fe(II) in rainwater from southeastern North Carolina (Kieber et al., 2001).

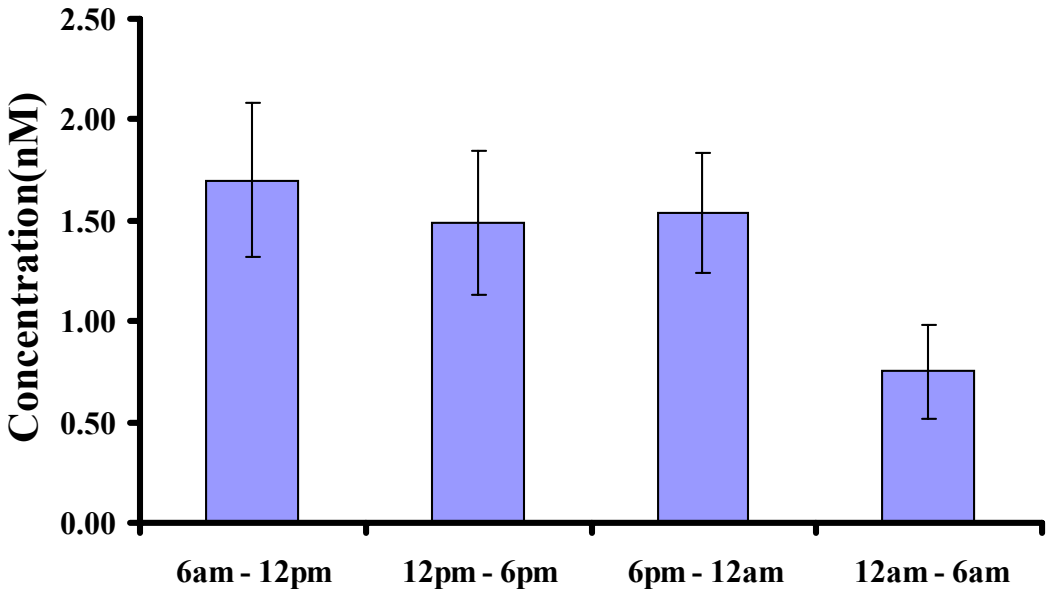


Figure 6. Volume weighted average and standard deviation for Cu(I) by time of day.

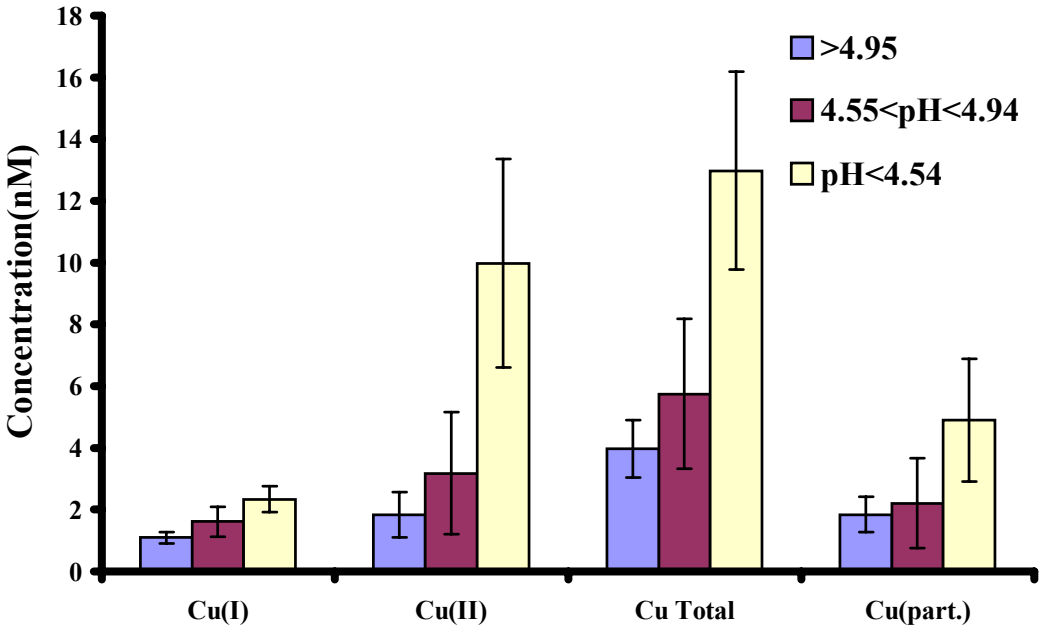


Figure 7. Volume weighted averages and standard deviations for Cu(I)(aq), Cu(II)(aq), total copper, and particulate copper at pH $\geq$ 4.95, 4.55 $\leq$ pH $\leq$ 4.94, and pH $\leq$ 4.54.

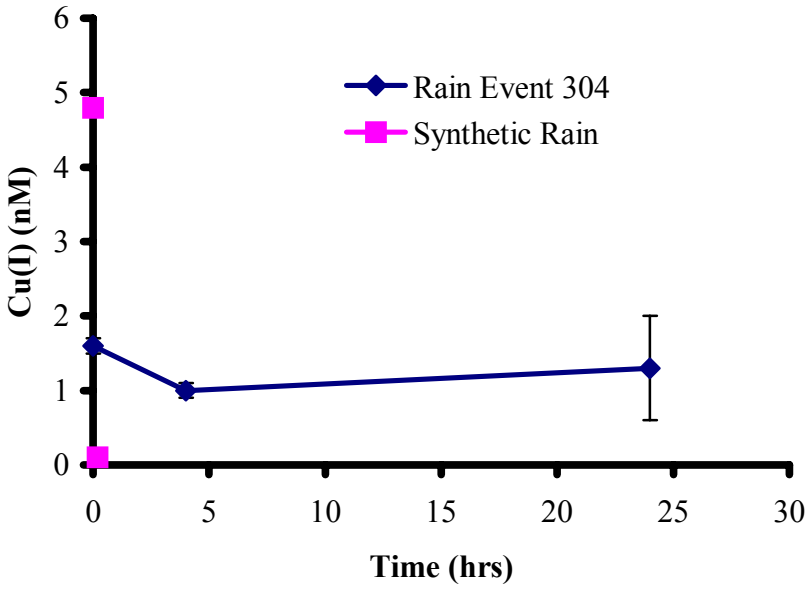


Figure 8. Synthetic rainwater spiked with 4.8 nM Cu(I) and extracted for Cu(I) within minutes. Authentic rainwater extracted for Cu(I) within minutes, after 4 hours, and after 24 hours.

Total dissolved copper (Cu(I) and Cu(II)) and copper-complexing ligand concentrations have been determined in Wilmington rainwater (Figure 9; Sutton, 2000). Conditional stability constants of $10^9 - 10^{12}$ were determined for copper-ligand complexes in these samples. Ligand concentrations were consistently lower than the dissolved copper concentrations, indicating that only a portion of the total dissolved copper in rainwater is strongly complexed. This analytical method does not distinguish between Cu(II) and Cu(I) ligands, and does not yield the exact structure of this ligand.

Mineql + Speciation Calculations

The Mineql+ speciation program (Schecher, 1994) was employed to assess copper complexation with other components in Wilmington, NC rainwater (Table 9). These calculations suggested that copper in rainwater exists as free Cu(II) ion, Cu(II)-oxalate complexes, and Cu(II)-histidine complexes (Figure 10). If the concentrations for these three forms of Cu(II) are summed they equal the Cu(II) concentration (all data) reported previously on Table 4. Mopper and Zika (1987) detected histidine concentrations (0.6 μM and 0.01 μM) in two of eight marine rains they analyzed. The authors determined that the most likely source of histidine and other amino acids in rain was biological and of surface seawater origin. Histidine was also detected in the sea surface microlayer and subsurface waters in Stony Brook Harbor, New York (Kuznetsova and Lee, 2002). In addition, these calculations indicate Cu(I) exists as the free Cu(I) ion and as a Cu(I)-chloride complex in rainwater, however, most exists as the free ion. As for Cu(II), if the concentrations of these two forms of Cu(I) are summed they equal the Cu(I) concentration (all data) reported on Table 4.

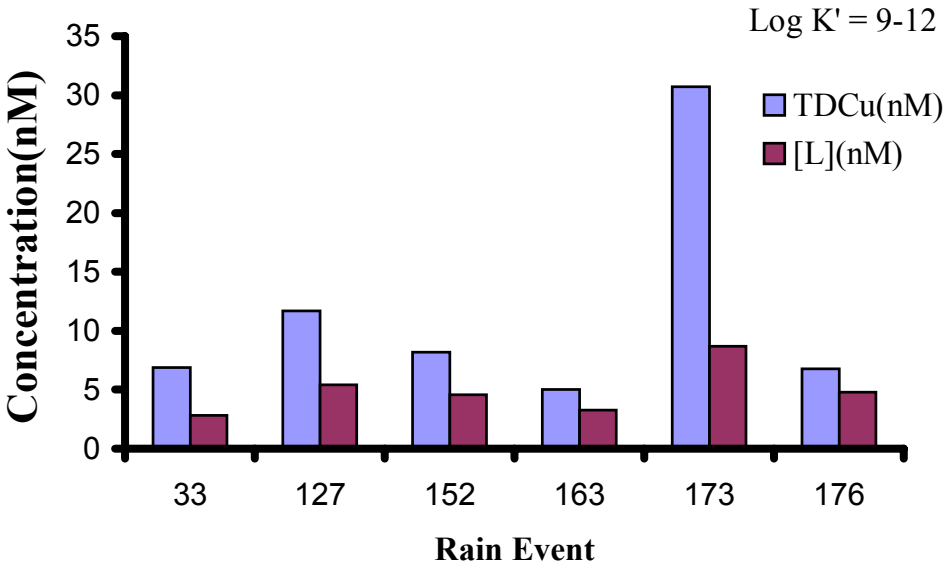


Figure 9. Total dissolved copper (TDCu) and ligand concentrations for selected rain events in Wilmington, NC. Data from Sutton (2000).

Table 9. Rainwater composition used in copper speciation calculations. The rainwater pH was 5.3, and it was assumed to be in equilibrium with air (log P_{CO2} = -3.5), so the concentration of CO_3^{2-} was 0.01 nM, too small to affect copper speciation in this rainwater. No complexation observed between Cu(II) and the amino acids glycine, valine, tyrosine, threonine, phenylalanine, methionine, lysine, leucine, isoleucine, glutamate, asparagine, and alanine when they were present at concentrations up to 1μM.

Matrix	μM	Organics	μM	Metals	nM
NO_3^-	12	Formate	10	Cu(I)	1.4
Cl^-	53	Acetate	7	Cu(II)	3.2
SO_4^{2-}	14	Oxalate	2	Fe(II)	40
Na^+	55	Histidine	0.1	Fe(III)	25
K^+	3			Cr(III)	1
Ca^{2+}	4			Cr(VI)	1
Mg^{2+}	3				
NH_4^+	9				
H^+	5				

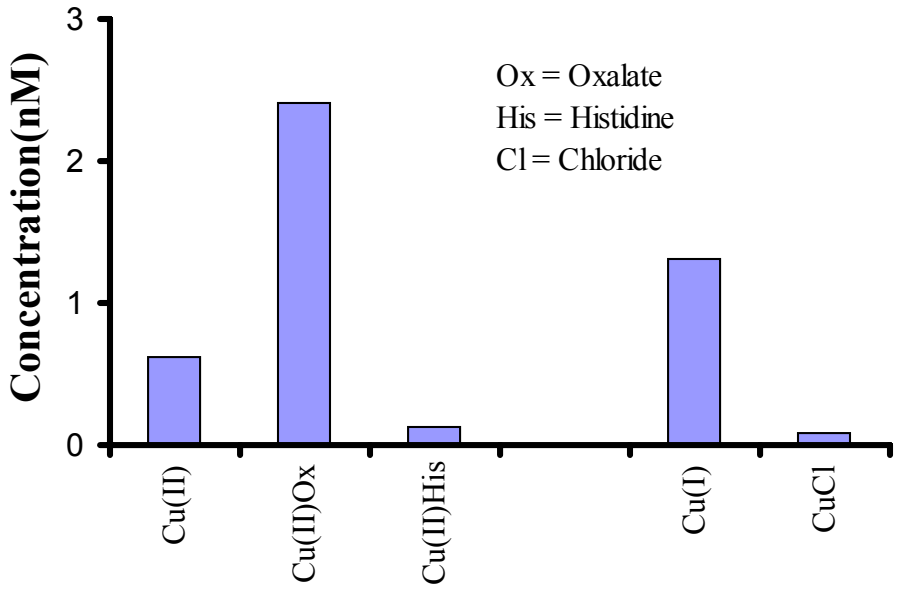


Figure 10. Possible complexes and concentrations for Cu(I) and Cu(II) in Wilmington, NC rainwater.

Estuarine Water

Samples were collected and analyzed for Cu(I) and total Cu during April, July, and November of 2001 and March 2002 (Table 10). C. Shank provided the total copper values (unpublished data). Average Cu(I) values ranged from 0.17 nM - 0.79 nM, whereas average total Cu values ranged from 6.8 nM - 17.4 nM. The percentage of total Cu that was Cu(I) varied from 1.9% - 4.1% with an overall average of 3.4%. This overall average matches well with what Moffett and Zika (1988) found in the Atlantic Ocean and Gulf of Mexico. They found Cu(I) comprises 5% - 10% of the total dissolved copper in surface waters. Copper(I) measurements in core incubation experiments showed there was no significant flux of Cu(I) into or out of the water overlying the sediments (Table 11).

Flux Calculations

Total copper concentrations found in Wilmington rainwater were 5.3 $\pm$ 0.9 nM (Table 4). The atmospheric wet deposition flux of copper was calculated to be 504 $\mu g\ m^{-2}\ yr^{-1}$. This flux matches closely with the 600 $\mu g\ m^{-2} yr^{-1}$ (June 1999 to July 2000) copper flux that Campos et al. (2001) determined for Florianopolis, Brazil, a coastal urban site. Scudlark et al. (1994) found slightly lower results at two Maryland Chesapeake Bay sites from June 1990 to July 1991. They determined a flux of 275 $\mu g\ m^{-2}\ yr^{-1}$ (Wye site) and 244 $\mu g\ m^{-2}\ yr^{-1}$ (Elms site).

In addition to the atmospheric flux of copper, riverine, oceanic, and sediment-water exchange copper fluxes were calculated (Figure 11). All fluxes are expressed in units of moles of Cu per year. Total copper values from C. Shank (unpublished data) were used to calculate the riverine, oceanic, and sediment-water exchange fluxes for

Table 10. Copper(I) and total copper concentrations (nM) for Cape Fear River Estuary samples collected during April 2001, July 2001, November 2001, and March 2002. Station 2 for April 2001 only had one total copper value that corresponded to a Cu(I) value. Total copper was not analyzed for the March 2002 experiment. Total copper values were provided by C. Shank (unpublished data).

Spring 2001	Cu(I) Range	Cu(I) Average	Total Cu Range	Total Cu Average	%Cu(I) Range	%Cu(I) Average
Station 1	0.34 - 0.86	0.49	13.4 - 15.8	14.4	3.2 - 4	3.7
Station 2	0.20 - 0.92	0.34	10.4	N/A	2.6	N/A
Summer 2001						
Station 1	0.37 - 0.70	0.58	16.4 - 18.6	17.4	2.9 - 4	3.4
Station 2	0.11 - 0.24	0.17	10.0 - 13	11.7	1.4 - 2.4	1.9
Fall 2001						
Station 1	0.14 - 0.64	0.33	8.5 - 11.8	10.2	2.7 - 7.5	4.1
Station 2	0.12 - 0.35	0.23	6.1 - 8.0	6.8	3 - 4.3	3.8
Spring 2002						
Station 1	0.46 - 1.3	0.79	N/A	N/A	N/A	N/A
Station 2	0.20 - 0.44	0.31	N/A	N/A	N/A	N/A

Table 11. Copper(I) concentrations in core incubation experiments using Cape Fear estuary sediments collected during April 2001, July 2001, November 2001, and March 2002. Calculated Cu(I) fluxes in units of nmol/m^2/day.

Spring 2001 Station 1	Cu(I) T_0	Cu(I) T_{final}	Flux
Core A	0.53	0.37	2.6
Core B	0.44	0.37	4.4
Core D	0.86	0.37	-5.1
Station 2			
Core D	0.26	0.92	12.5
Core G	0.22	0.4	4.2
Core F	0.2	0.22	0.9
Summer 2001 Station 1			
Core B	0.55	0.46	1.2
Core C	0.70	0.62	1.3
Core D	0.68	0.70	2.7
Station 2			
Core A	0.18	0.13	0.00
Core B	0.22	0.11	-1.1
Core C	0.11	0.20	1.8
Fall 2001 Station 1			
Core A	0.29	0.26	3.4
Core B	0.33	0.37	4.6
Core C	0.64	0.26	-4.7
Station 2			
Core A	0.26	0.15	0.4
Core B	0.24	0.35	5.4
Core C	0.26	0.20	1.5
Spring 2002 Station 1			
Core A	1.3	0.46	-14.7
Core B	0.95	0.75	-1.9
Core C	0.86	0.62	-2.7
Station 2			
Core A	0.37	0.29	-1.8
Core B	0.31	0.22	-2.0
Core C	0.44	0.20	-5.1

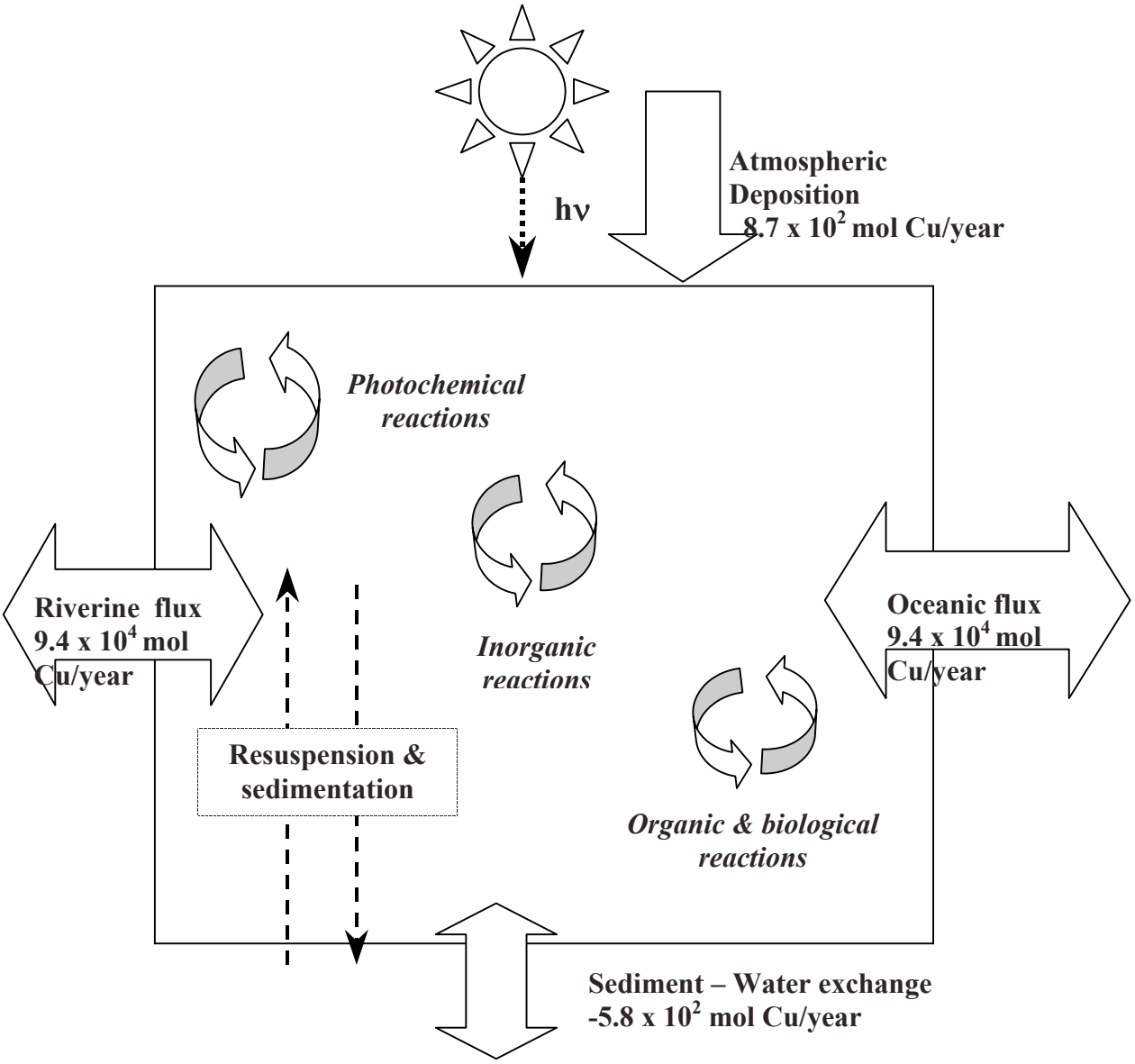


Figure 11. Estuarine box model for the Cape Fear system. Copper fluxes (moles Cu/year) for atmospheric deposition, riverine and oceanic input, and sediment-water exchange.

copper. Almost the same amount of copper that enters the estuary from atmospheric sources (8.7×10^2 moles Cu/year) then fluxes into the sediments (5.8×10^2 moles Cu/year). The riverine and oceanic flux (9.4×10^4 moles Cu/year) is the same because total dissolved copper (18 nM) is conservatively mixed among different salinities (Shank, 2003).

CONCLUSIONS

1. Total copper concentrations in rain did not significantly vary between the seasons. In southeastern North Carolina rainwater copper(II) concentrations were significantly higher in the summer due to the oxidation of Cu(I), whereas Cu(I) concentrations were significantly higher in the winter due to the reduction of Cu(II).
2. All copper species (Cu(I), Cu(II), Cu_{total}, $Cu_{particulate}$) were higher for storms of continental origin versus storms of coastal origin.
3. Strong positive correlations were found between Cu(I) and DOC, NO_3^-, SO_4^{2-}, Fe_{total}, and $Fe_{particulate}$. An inverse correlation was found between Cu(I), Cu(II), Cu_{total}, $Cu_{particulate}$ and rainwater amount.
4. No diurnal variations were seen with Cu(I). However, Cu(II) concentrations showed a peak between 12 pm and 6 pm.
5. All copper species (Cu(I), Cu(II), Cu_{total}, $Cu_{particulate}$) increased in concentration with decreasing rainwater pH.
6. Cu(I) is more stable in authentic rain than in synthetic rain. Undetermined ligands may be stabilizing Cu(I) in authentic rain.

7. For Cu(II) complexation, thermodynamic Mineql+ calculations suggest the Cu(II) free ion, Cu(II)oxalate, and possibly Cu(II)histidine are the important species formed at a realistic rainwater pH. These calculations suggest Cu(I) exist as the free ion and is possibly bound to chloride.
8. In estuarine water, the percentage of total Cu that was Cu(I) varied from 1.9% - 4.1% with an overall average of 3.4%. No flux of Cu(I) was observed into or out of the water overlying the estuarine sediments.
9. The calculated atmospheric flux of copper is in good agreement with the calculated copper flux in Florianopolis, Brazil and two Maryland Chesapeake Bay sites.
10. Almost the same amount of copper that enters the Cape Fear River estuary from atmospheric deposition (8.7×10^2 moles Cu/year) fluxes into the sediments (5.8×10^2 moles Cu/year).